PB-246 833-T

THE EXPERIMENTAL TOXICOLOGICAL CHARACTERISTICS OF THE BASIC PRODUCTS OF THE SHALE CHEMICAL INDUSTRY

E. A. Blinova, et al

Environmental Protection Agency
Research Triangle Park, North Carolina

August 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

324210

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA TR 76-55	2.	PB 246 833-T

4. Title and Subtitle

The experimental toxicological characteristics of the basic products of the shale chemical industry.

5. Report Date: 1972

6.

7. Author(s): E. A. Blinova and H. Janes

8. Performing Organization Rept. No.

9. Performing Organization Name and Address: Translatedfrom the Russian by the EPA

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address: EPAISD, Translations Section, Research Triangle PArk, N.C. 27711

13. Type of Report & Period Covered

14.

15. Supplementary Notes

Nauchno-Prakticheskaya Deyatel'nost Inst. Eksper. Klin. Med. Tallin,1972, 41-48

16. Abstracts

17. Key Words and Document Analysis. 17a. Descriptors

EPAISD
Environmental Health

17b. Identifiers/Open-Ended Terms

Soviet Union
Russian
Oil shale

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

17c. COSATI Field/Group 06-T 68G

PRICES SUBJECT TO CHANGE

18. Availability Statement: This translation was made from a non-copyrighted text.

Libby Smith

19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 13
20. Security Class (This Page) UNCLASSIFIED	22. Price 3.50-2.25

324210

TR 76-55

THE EXPERIMENTAL TOXICOLOGICAL CHARACTERISTIC OF THE BASIC PRODUCTS OF THE SHALE CHEMICAL INDUSTRY [Eksperimental'no-toksikologicheskaya kharakteristika osnovnykh produktov slantsekhimicheskoy promyshlennosti]

by

E.A. Blinova and H. Jänes

Published in Nauchno-Prakticheskaya Deyatel'nost Instituta Eksperimental'noi i Klinicheskoi Meditsiny, Tallin, 1972, pp. 41-48.

From the toxicological point of view, the products of thermal processing of shale (tars and phenols) are complex multi-component mixtures made up mainly of various types of hydrocarbons and they are of a phenol type which have an effect in case of inhalation--due to volatile components, and an effect on the skin due to the entire complex of compounds. Physically this liquid is of a dark color with a sharp specific odor.

The shale industry produces tars of two types. Tar with low-temperature decomposition of shale (semi-coking at 500° C) is produced in shaft generators, tunnel-type annealing furnaces and in equipment with

---

Translated for NERC-Library, EPA, from the Russian by LEO KANNER ASSOCIATES, P.O. Box 5187, Redwood City, California 94-63, (415) 365-3046, August 1975.

solid heat-carrying agents. These tars contain paraffin, naphthene, olefin and aromatic hydrocarbons, neutral and acetic oxygen, sulfur and nitrogen compounds (see Figure 5 [sic] Figure 1).

The tar of high-temperature decomposition of shale (coking at 1200° C) is produced in compartment-type furnaces. This tar differs noticeably from the tars of low-temperature decomposition of shale--it contains aromatic hydrocarbons [2, 8] in a significant quantity (up to 53%).

The physical and chemical and the chemical group composition of shale tars depend on the boiling point of the tar. Fractions which boil away at a lower temperature contain up to 70% unsaturated hydrocarbons. In high-boiling fractions, the content of phenols and neutral oxygen compounds increases.

The shale phenols of tar waters are obtained in mills for dephenolization by a method of extracting them with butyl acetate from waste waters which form during processing of shales. According to chemical composition, the phenols of tar water consist mainly of diatomic phenols and have the corresponding dimethyl-resorcin empirical formula $C_8H_{10}O_2$. According to the data of B.I. Ivanov [6] and Yu. Lillye and Kh. Kundel' [7] the group component of this type of phenol is characterized by the presence of phenol, cresols, xylenols, alkyl derivatives of resorcin. The fractions of monatomic shale phenols and fractions of diatomic shale phenols of tar waters are obtained during distillation of the total water soluble phenols with boiling temperature 180°--270° C for the first and 271--315° C for the second. Tar shale phenols are obtained from shale oil tars by a method of extracting them with alkali. Shale tar phenol fraction 270°--320° C, insoluble in water,

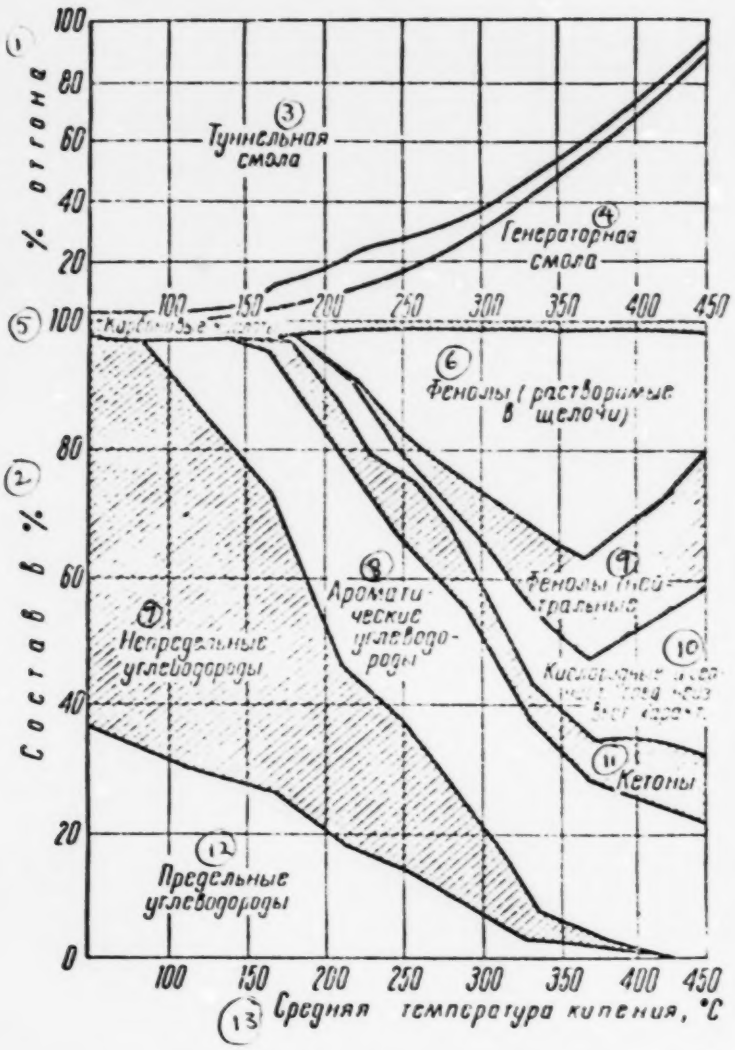

Figure 1. Fractional and Chemical Group Components of Shale Tar (According to A. Ya. Aarnye [1]).

Key:
1. % distillate
2. Component in %
3. Tunnel tar
4. Generator tar
5. Carboxylic acids
6. Phenols (soluble in alkali)
7. Unsaturated hydrocarbons
8. Aromatic hydrocarbons
9. Phenols (neutral)
10. Oxygen and sulfur compounds of unknown character
11. Ketones
12. Saturated hydrocarbons
13. Average boiling temperature, ° C

are a mixture of alkylated oxy and dioxy products of benzene and napthalene.

Absolute toxicity of low-boiling fractions of shale tars is considerably less significant than the toxicity of high-boiling fractions. For example, during inhalation innoculation of white mice with average-lethal concentrations of volatile components for the lungs, the tars of equipment with solid heat-carrying agent is 62±3 mg/ℓ, and for average-heavy tars --16+2 mg/ℓ. But low-boiling fractions possess greater volatility than high-boiling fractions (a difference of 10 times). Therefore, the actual production danger of poisoning with volatile components of light (low-boiling) fractions is higher than that of heavy fractions.

With semi-coking of shale fuels in various equipment, the tars obtained have a non-uniform fraction composition and in connection with this, possess non-uniform toxicity. Low-boiling fractions are contained in a significant quantity in tars of tunnel-type furnaces and units with solid heat-carrying agents. The relative toxicity of the tar depends on this: the volatile components of chamber and generator resin are more toxic than the volatile components of the aforementioned tars (see Table 1).

Shale tars of the Baltic region are complex mixtures of various organic compounds inasmuch as they contain up to 25--30% phenols. By comparative tests it has been clarified that the average-lethal concentration of volatile components of non-dephenolized diesel fractions of shale tar for white mice is 16.5±0.27 mg/ℓ, and for dephenolized--19.5±0.43 mg/ℓ. With peroral introduction, the appropriate factor for

TABLE 1 LIMITS OF BOILING, ABSOLUTE AND RELATIVE TOXICITY OF VOLATILE COMPONENTS OF ESTONIAN SHALE TARS FOR WHITE MICE

Type of Tar	Limit of Boiling		Toxicity	
	Beginning of Boiling, ° C	Up to 350° C % of Volume Evaporating	50 mg/ℓ	Relative
Compartment resin	150-180	60.3--62.0	39±1.5	1.0
Resin of equipment with solid heat-carrying agent:				
Light fraction	73	87.0	63±3.0	0.5
Average-heavy fraction	189	50.0	16±2.0	2.1
Tunnel tar:				
Average fraction	192-215	76.5	66±3.5	0.4
Generator tar	130	47.0	27±1.4	1.2
Diesel fraction of total tar	180	96.0	15±0.3	2.6

white rats with non-dephenolized tar equals 5.8±0.3 g/kg, and with dephenolized--10.0±0.4 g/kg. Thus, all the component parts of the shale tar introduced have a toxic effect, but the leading role is played by phenol compounds which to the greatest degree determine the toxicity of these tars.

Shale phenols with inhalation intake cause, in the test animals, dyspnea, flabbiness, hyperemia of the mucous membranes; with higher concentrations one observes a sideways position of the body, spasms and fatal results.

The toxic effect of vapor and gaseous mixtures of shale phenols is determined by the combined effect of its component parts. By a method of gas chromatography one can identify in the composition of volatile components of shale phenols of tar waters fed into the experimental innoculating chamber, up to 73% 5-alkyl derivatives of resorcins; in

smaller quantities one observes monatomic phenols, dimethyl phenols, resorcin and its residual alkyl derivatives.

Lethal concentrations of vapors of shale phenols (according to their total) for white mice ammounted to 1.7 mg/ℓ for tar phenols (see Table 2) [9]. The higher toxicity of volatile components of shale phenols in comparison, for example, with the phenols obtained from coal tars [3, 4], probably, is explained by the individual component of phenol compounds which are in the air medium.

Considering the multi-component character and extreme scattering quantitatively of individual representatives of the phenol type of the mixture, the most probable standard for volatile components of shale phenols must be made according to the phenol which appears in the mixture in the largest quantity (5-methyl resorcin).

TABLE 2 TOXICITY OF SHALE PHENOLS WITH INHALATION AND PERORAL METHODS OF INTAKE

Types of Phenols	Boiling Range ° C	LD50 Phenols for White Rats mg/kg	Lethal Concentrations of Shale Phenols with Inhalation mg/ℓ
Shale phenols of tar waters	180-310	765±70* 2320±214**	0.5 (absolute)
Monatomic shale phenols of tar waters	180-270	386±42*	
Diatomic shale phenols of tar waters	270-310	633±73*	
Tar shale phenols	270-310	3000±230**	1.7 (absolute)

*--solvent--water
**--solvent--oil

According to classifications of S.D. Zaugol'nikov, A.O. Loyta, A.M. Ivanitskiy [5], the volatile components of generator and compartment

tars, and also the average-heavy fraction of the tars of units with solid heat-carrying agents are of average toxicity and the volatile components of average fractions of tunnel tars and light fractions of tar of units with solid heat-carrying agents--are less toxic substances. With peroral introduction, the shale tars are also low-toxic substances. With peroral introduction of shale phenols, there is a significantly noticeable difference in lethal doses depending on the solvent used (water or oil).

When comparing the values for lethal result for introducing phenols using one or another solvent, the greater toxicity is indicated with monatomic shale phenols.

The toxicity of total shale phenols of tar waters in diatomic shale phenols of tar waters is of a single order and the lower fractions of monatomic phenols, probably is due to the percentage prevalence of diatomic phenols in the total phenols.

The lower toxicity for shale phenols obtained by an enteral method of intake, in comparison with inhalation (III B and IV A charges of toxicity according to the classification of S.D. Zaugol'nikov with co-authors, [5]) probably is explained not only by the difference in the fractional composition of the phenols but also depends to some degree on the method of introduction of the substance (see Table 2).

By experimental research it was established that all shale tars and phenols produced in the Estonian SSR are characterized as irritants, and in a longer time period affect the skin. Repeated application of shale tars and phenols causes the development of contact dermatitis of a serous-exudate character and with greater concentrations--necrosis

in the test animals.

All types of tars in long term tests (16 weeks) cause development of small warts on the skin, in later time periods--papillomas and cancerous skin tumors develop as a result of shale compartment resins in white mice.

In decreasing force of irritating effect on the mucous membranes (conjunctiva of rabbits), the shale tars are placed in the following order: generator, compartment tar and tunnel tar, and also tar of equipment with a solid heat-carrying agent. The shale tars did not cause in the test animals irreversible pathological changes of the conjuctiva, corneas and sclera.

In tests on guinea pigs, the data obtained indicate that Estonian shale tars are relatively weak exoallergins which with repeated contact however can cause sensitization of the organism. The phenomena of group allergy which is important in the experiment is explained by the closeness of chemical composition of the various shale tars. As to the changes in reaction of the organism the most important factors are the nonphenol compounds of the shale tars in the composition.

The sensitizing character of the effect is established in turn in the tar shale phenols when they affect the skin of guinea pigs.

The skin-resorptive effect of shale tars and phenols is apparent in changes of a number of integral factors of the organism (body weight, nerve-muscle excitability, etc.).

A chronic picture of intoxication with inhalation of the most toxic product--shale water-soluble phenols--in a dose subliminal to short-term effect is accumulated mainly due to the non-specific reaction

of the organism.

As to the central nervous system, one notes a persistent dominance of inhibiting processes, the functions of the thyroid gland are depressed, a breakdown in existing and potential reserves of the adrenal cortex were apparent (glucocorticoidal function) with the retention of changed reaction in the regenerative period. A certain weakening of the immune reaction of the organism was observed. As to the specific changes, the largest factor is breakdown in porphyritic metabolism, however, with the reverse phenomena apparent in the regenerative period.

The functional state of the liver is basically in normal limits, unstable changes were noted only by using highly sensitive tests (bromsulfphthalein).

In considering the general tendency toward lung disease in experimental rats of a type of focal parabronchial pneumonia, a larger affliction of this type of pathology was noted in the test animals in comparison with the control.

The assortment of chemical commercial products on a base of shale oils resins and phenols is fairly broad. It includes fuel products (shale fuel oil and gasoline), a varied assortment of varnishes and mastics ("kukersol" varnish, LSP-1, bitumen-kukersol mastic, SFM-2, DFK-10 resins and others) used as solvents and glue materials, and also substances for electrical and electronic industries, rubber, etc. (Shale epoxy resin, phenol pitch, polygraphic drying oil). Moreover, a whole series of products which have more specific uses exist: a vegetation growth stimulator, SRV-1, a shale tanning agent for treating leather, phenolin (for the medical treatment of ring worm) etc. The types of

products mentioned above are either products of thermal processing of shales and resins (shale gasoline), or are mixtures of separate fractions of resin and phenols (bitumen-kukersol mastic) or are condensations of the basic product with other chemical compounds (SFM-2 resin).

Formaldehyde is most often used as an auxiliary chemical material; less often epichlorohydrin, colophony and others are used. The characteristic effect on the organism of the commercial products of the shale industry basically is determined by the toxicity of the basic components. The toxic phenomena involve damage of the nervous system, and when acute have a narcotic and irritating effect. An evaluation made on the class of toxicity involved introducing 14 of the samples being studied of commercial products [9] to a group of average or low-toxic substances; included were shale solvent added to a number of highly toxic substances. The least toxic substance, a vapor of gaseous mixture which did not cause fatal results in experimental animals, is polygraphic drying oil "P," SFM-2 resin. The results of effect on skin of substances studied corresponds to the degree of toxcitiy during inhalation.

The most acute skin-resorptive effect was apparent when studying "Kukersol" varnish and solvent. The sharp unpleasant ordor apparent in the products made on a shale oil base makes it impossible to use them in living quarters.

The actual danger of occurrence of toxic phenomena due to volatile components of the samples of the products being studied increases sharply with heat which is important in industry for obtaining this product and also in a number of cases when using them.

BIBLIOGRAPHY

1. Aarna, A. Ya., "Shale resin as a new material for obtaining antiseptics", Tr. nauchno-tekhn. soveshchaniya po primeneniyu slantsevykh produktov dlya bor'by s vresitelyami, boleznyami i sornyakami sel'skokhozya stvennykh rasteniy. [Works of the scientific conference on the use of shale products for combatting harmful, diseased and weed growth in agriculture]. Tallin, 1956, 17-20.

2. Barshevskiy, M.M., Bezmozgin, E.S., Shapiro, R.N., Spravochnik po pererabotkye goryuchikh slantsev [Handbook on processing shale fuels], Leningrad, 1963.

3. Vrednyye veshchestva v promyshlennosti, chast' I, Organicheskiye veshchestva, [Harmful substances in industry, Part I, Organic substances], Under the general edit. of N.V. Lazarev, 1963, 313-331.

4. Grigor'yev, Z.E., "Toxicity of gas resin of semi-coked cherry coals and its fractions". In coll.: Inform. biol. Len. in-ta gig. tr. i prof. zabolevaniy. Ref. rabor za 1951, 53-55.

5. Zaugol'nikov, S.D., Loyt, A.O., Ivanitskiy, A.M., "Toxic-hygienic classification of harmful substances." In the book: Printsipy i metody ustanovleniya predel'no dopustimykh kontsentratsiy vrednykh veshchestv v vozdukhe proizvodstvennykh nomeshcheniy, [Principles and methods of establishing maximum permissible concentrations of harmful substances in the air of production rooms], Moscow, 1970, 76-83.

6. Ivanov, B.I., "Methods of purifying waste waters of shale production and the chemical composition of phenols", Mater konfer. po ochistkye fenol'nykh stochnykh vod. [Materials of the Conference on purifying phenol waste waters], Moscow, 1960, 18-28.

7. Lillye, Yu., Kundel', Kh., "The chemical composition of shale phenols of tar water", Slantsevaya i khimicheskaya promyshlennost', 1967, 6, 17-21.

8. Sinteticheskiya moyuchchiye veshchestva iz slantsevoy smoly, [Synthetic cleaning substances made of shale resins], Tallin, 1964.

9. Toksikologiya slantsevykh produktov. Metodicheskoye pis'mo. [Toxicology of shale products. Method letter], Tallin, 1970, (Inst. of Exper. and clinic. med., Moscow Public Health Dept., Est. SSR).